

FY2003 Report

Title: **Discrete and Continuum Absorption Parameters for Water Vapor in the Midinfrared**

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Research Objectives

New measurements of the water-vapor continuum absorption are being undertaken using long-pathlength FTIR spectroscopy, linear laser absorption spectroscopy, and laser cavity-ringdown spectroscopy in support of the AIRS, HIRDLS, and TES missions. The laser measurements are being made in the 9 to 11 micron region using a tunable microwave-sideband carbon-dioxide-laser infrared source. These efforts include detailed measurements of the density and temperature dependence of the continuum, building on our previously published work (Tobin et al., 1996). These same techniques will also be applied to the accurate measurements of halfwidths and pressure shifts and their temperature dependencies, with special emphasis given to the shapes of the far wings of the water-vapor lines.

I. PROGRESS AND RESULTS SUMMARY

A. Continuum Absorption in H₂O at 10.6 μ m

The water-vapor continuum plays an important role in the Earth's radiative balance. Despite its importance, there have been a rather limited number of laboratory measurements in the 9-11 μ m (Peterson, 1979, Nordstrom, 1978, Arefev, 1977, McCoy, 1969) as a result of small magnitude of the absorption (10^{-6} /cm) and its diffuse nature which lacks any clear spectral signature. Hinderling (Hinderling, 1987) have surveyed the published values of the water vapor continuum coefficients of self-broadening and have reported uncertainties on the order of ± 35 %. A more comprehensive comparison of both field and laboratory measurements was given by Grant (Grant, 1990) who reported uncertainties of ± 20 %. Until recently, these measurement have made using of long pass cells (White cells) and consequently, have required large absorption cells to attain the necessary sensitivity. The recent introduction of cavity ringdown techniques (Romanini, 1996) have provided an important new tool that overcomes the need for large cells while retaining sufficient path lengths. For example, Cormier (Cormier, et al. 2002) have reported self-broadening coefficients of water vapor continuum at three different CO₂ laser lines using CRDS equipped with a 6 liter cell having an effective path of ~ 1 km. Their published results are in excellent agreement with the White cell results and are in good agreement with the far-wing line shape theory of Ma and Tipping (1995,1999). Although offering great promise, the number of measurements reported in the mid-infrared is limited to the wavenumbers of fixed CO₂ laser lines which are not always optimal for avoiding local line absorption. We recently reported the development of a microwave-tunable CRD spectrometer that overcomes this problem (Bucher, 2000). The results reported here were obtained using this new instrument.

We have undertaken a series of studies to measure the continuum absorption of H₂O in the 10 μ m region. As a result of the weak and diffuse nature of the absorption, we had hoped to provide redundancy checks of the results by performing measurements using cavity ringdown spectroscopy (CRDS) and linear absorption spectroscopy in White cells coupled to both an FTIR spectrometer and a CO₂ laser. To date, we have not achieved the necessary sensitivity for continuum measurements using either of these latter two linear absorption methods. Therefore, our report includes only data obtained using the CRDS although considerable effort will continue to be directed towards the validation of these data using a second independent method based on White cells.

The mid-infrared cavity ring down spectrometer has been described in detail elsewhere (Bucher, et al. 2000) and has undergone a number of modifications to improve its stability. Briefly, the spectrometer is based on coupling a microwave-tunable (8-18 GHz) sideband of the CO₂ carrier frequency into a 1.2 m long confocal resonator. The near confocal resonator cavity is equipped with two mirrors having reflectivity of 99.5%. A PIN diode switch is used to rapidly turn off the light to the cavity and the resulting decay is monitored using a fast HgCdTe detector (50 MHz band pass) and digitally stored. High

repetition rates of 10 kHz are possible using this technique and are currently limited by the storage capacity of the digital scope. The total volume of the cell is 2 liters. This small volume permits rapid exchanges (<1 min) of the gas within the cell and therefore, minimizes systematic errors associated with thermal drift of the spectrometer. Water vapor pressures are measured with a capacitance manometer and simultaneously recorded with the ring down data.

The total decay rate, $k_{RDC}(_)$, of the CRD cavity is sensitive to sum of the following contributions,

where L is the cavity mirror separation, R the reflectivity of the mirrors and c is the speed of light. The first term represents the cavity loss due to mirror reflectivity. $k_w(_)$ is the absorption coefficient of the gas and $k_{bg}(_)$ accounts for other loss factors such as Rayleigh scattering and/or contamination from trace gases.

The following absorption rate dependence on temperature and pressure has been used to model the continuum absorption,

where N_0 is the number density of an ideal gas at the reference conditions (mol cm^{-3}), C_s and C_f are the continuum coefficients for self-broadening and foreign gas broadening, respectively ($\text{cm}^2 \text{ atm}^{-1} \text{ mol}^{-1}$), e and P_f are the water vapor and foreign gas pressures (atm).

Because of large electric-dipole moment of H_2O , the self-induced continuum absorption dominates and therefore the initial studies reported here are on pure water vapor. However, for reasons that will become clear below, we are currently obtaining water continuum data in N_2 at 1 atm.

A representative trace of the ring down signal obtained in 1 sec from an average of 500 decay events is shown in Fig. 1. The empty cavity decay time is 0.704 usec. The data are well fit to a single exponential over a region of ~ 4 usec as illustrated in the bottom of the figure by the residuals magnified by 10-fold. This time period corresponds to an optical path length of >1 km.

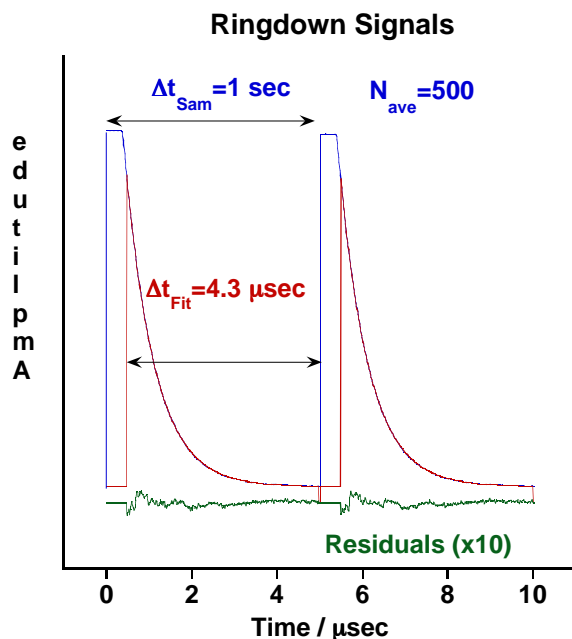


Figure 1. Ringdown signals and fits

The data shown in Fig. 2 is typical of type of the sensitivity and reproducibility we have obtained for 5 different regions examined. The absorption rate data are shown as a function of time (~20 min) during which the cell pressure was twice increased from 0 to 15 Torr with water vapor and then pumped out. The spectral region examined is at 945.513 cm^{-1} [$10\text{P}(18) + 15.991 \text{ GHz}$] where the contribution from local line absorption over this pressure range is negligibly small ($<10^{-8} \text{ cm}^{-1}$). The lower trace represents the vapor pressure of H_2O vapor in Torr.

From Eq. (2) above, the continuum absorption should scale with the square of the H_2O partial pressure. It is clear from Fig. 2 that this required pressure dependence is not seen in our data even though the absorption rate we observe is the right order of magnitude ($C_s = 4.32(2) \times 10^{-22} \text{ cm}^2 \text{ atm}^{-1} \text{ mol}^{-1}$). This is more clearly illustrated in Fig. 3 where we explicitly show the pressure dependence of the absorption rate. (The larger scatter near zero pressure is a result of the pressure difference between the cell and the point of measurement). The data in this figure as well as for the other regions examined are much better fit to a straight line.

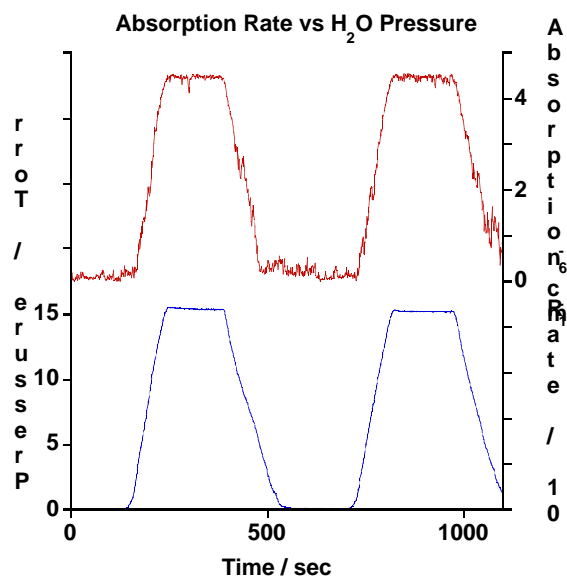


Figure 2. H₂O absorption vs time at 945.513 cm⁻¹

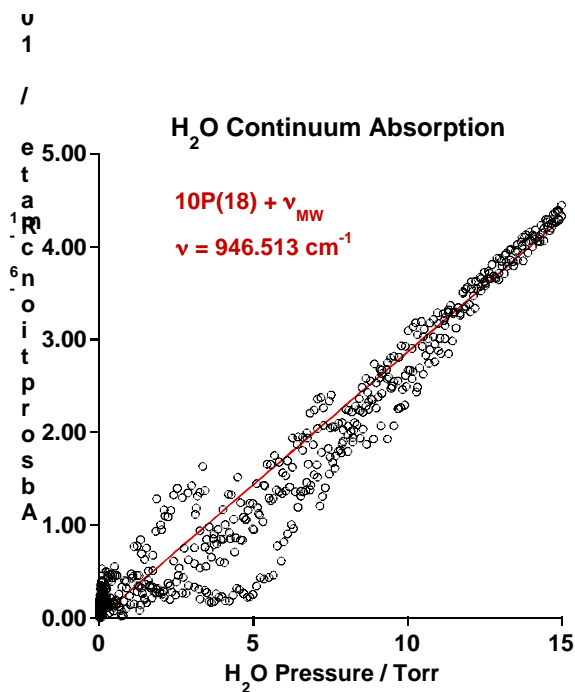


Figure 3. Absorption rate verses H₂O pressure

Although the reason for this discrepancy has not yet been resolved, it believed to be associated with Rayleigh scattering loss by water. For example, we have noticed linear increases in the ringdown rate as a function of Ar gas pressure. The scattering loss is

expected to be linearly dependent on number density and must be taken into account prior to obtaining absorption coefficients. It should be pointed out that all prior measurements have been done in N₂ where the contributions from scattering is present in both sample and background runs. Therefore, we are currently investigating these same spectral regions in H₂O/N₂ mixtures in anticipation of resolving this discrepancy.

II. PLANNED STUDIES

A. H₂O continuum absorption in N₂ mixtures

As we have found large discrepancies well outside the reproducibility of our measurements of the water continuum at room temperature with the previous results extracted from H₂O/N₂ mixtures, we plan to perform studies of H₂O in N₂ mixtures for direct comparison with prior results for a large number of regions in the mid-infrared.

B. H₂O lineshape studies in the mid-infrared using CRDS.

The high precision (<5 kHz) and tunability of the sideband spectrometer (many GHz) makes it useful for lineshape studies of water lines in this region at variable pressure conditions. These measurements will be used to validate the operating performance of the FTIR for lineshape measurements.

III DATA MANAGERMENTS/ARCHIVAL STRATEGY/ACCOMPLISHMENTS

As an important part of the experimental investigation of the continuum absorption of H₂O, we have developed an interactive Windows program for direct comparison of experimental data with the latest HITRAN database information. The program includes features to vary partial, total air pressure and temperature for various molecules listed in the HITRAN database using trackbars. Changes to simulated spectra (absorption or transmission) are therefore updated in real time. These features are extremely useful for modeling spectra and for comparison with experimental data under various laboratory conditions. Although the interface to HITRAN is a fairly recent addition, descriptions of other features of this software are given at

<http://physics.nist.gov/Divisions/Div44/facilities/uvs/jb95userguide.htm>

We also plan to provide the water continuum coefficients and the O₂/CO₂ data in cross section form to the HITRAN database when it becomes available.